

Self-Assembly and Waterlike Anomalies in Janus Nanoparticles

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(Dated: April 29, 2015)

Abstract

We explore the pressure versus temperature phase diagram of dimeric Janus nanoparticles using Molecular Dynamics simulations. The nanoparticle was modeled as a dumbbells particle, and have one monomer that interacts by a standard Lennard Jones potential and another monomer that is modeled using a two-length scale shoulder potential. Monomeric and dimeric systems modeled by this shoulder potential show waterlike anomalies, and we investigate if a Janus nanoparticle composed by one anomalous monomer will exhibit anomalous behavior and self-assembly structures. The influence of the non-anomalous monomer in the dimeric system properties was explored. We show that the diffusion anomaly is maintained, while the density anomaly can disappear depending on the non-anomalous monomer characteristics. As well, the self-assembled structures are affected. Our results are discussed in the basis of the distinct monomer-monomer interactions and on the two-length scale fluid characteristics.

I. INTRODUCTION

The understanding the structural and thermodynamical behavior of colloidal systems is important due to their applications in medicine, catalysis, production of photonic crystals, stable emulsions and other materials¹⁻³. The self-assembly structures of colloidal systems are very important to understand biological and chemical systems, like proteins and solutions⁴. Experimental and computational researches show that Janus spheres present cluster formation and properties different from bulk systems^{5,6}. When structured in equilibrated aggregates, the charge asymmetry of each particle is preserved⁵.

One of the relevant characteristics of colloidal solutions is the formation of stable self-assembly structures not present in traditional molecular systems^{7,8}. The variety of the length scales and geometry of the self-assemblies originate from the different types of potential energies involved and from the shapes of colloidal particles such as disk, spheric, rod-like and dumbbells.

The dumbbell shape is quite particular. Each dumbbell is a dimer formed by two spheres with the same diameter that overlap with a separation that varies from an almost total overlap to one or two monomer diameters. If each monomer of the dumbbell interacts with the other monomers by a one length scale potential such as the Lennard Jones potential the pressure temperature phase diagram resembles the diagram of the monomeric case⁹. If, however, each monomer of one dumbbell interacts with the other dumbbell by a two length scale potential, the symmetry breaks and a phase in which the dimers are aligned similar to a liquid-crystal phase appears⁹. The dumbbells diffuse along this line while no transport between the lines is observed. One special type of dummbbell is the Janus particles¹⁰. They are characterized by having two types of monomers. For instance one hydrophobic and the other hydrophilic. In this case the breaking of the spherical symmetry leads to a more complex set of phases. The hydrophilic monomers attract each other while the hydrophobic monomers repeal forming lamellar and micellar agregates of different length scales. The presence of this type of structures is not new in the literature. Systems with competing interactions, first neighbors repulsion and second neighbors attraction exhibit these same lamellar and micellar formations^{11,12} as observed in the Janus particles. One particular example where this type of interactions appear is in the mixture of water, oil and surfactant¹².

Recently, nanocomposites of dumbbells and Janus-type particles have been synthesized in large scale using several techniques, as physical vapor deposition¹³. These asymmetric colloidal dimers can be obtained through deposition of gold nanoparticles^{14,15}, phase separation and immobilization in liquid-liquid or liquid-gas interfaces¹⁶, using the interfacial activity of reverse micelles and microemulsions¹⁷ and other techniques.

Due to the resemblance between Janus particles and competing interaction systems, Janus dumbbells behave as surfactant in water-based emulsions due its amphiphilic properties^{18–20}. It has been shown that Janus particles are efficient in hydrophobization of textile materials, that depends on the size of the particles²¹. By a simple geometrical change, varying from spherical symmetric to cylindrical structural shapes, particles with new properties can be created⁴.

Simple models found rich pressure versus temperature phase diagrams and critical behavior of dumbbells and charged colloids^{22,23}. Varying the interaction potential, lamellar structures and gas-liquid phase separation are found in Janus particles^{24,25} in a very similar facion as in the competing interaction models these phases were found in the past¹². Micellization and phase separation also are related in such models²⁶. Homogeneous crystal nucleation of colloidal hard dumbbells can be suppressed by high free energy barrier or slow dynamics²⁷. Controlling the attractive of patchy colloids, liquid-gas separation can be suppressed and a gel phase can be formed²⁸.

Recently, the production of silver-silicon (Ag-Si) hybrid Janus dimmers was reported¹³. While silver is a material that do not shows anomalous behavior, silicon is classified as a anomalous fluid. Anomalous fluids exhibit a set of properties called anomalies that divert from the observed in simple fluids. The increase of density with the temperature at a fixed pressure and the increase of diffusivity under compression are examples of these anomalies. Water is the most well known fluid that present thermodynamic, dynamic and structural anomalous behavior^{29–31}, with 72 known anomalies³². In addition, silicon³³ and others material, as silica^{34–36}, Te³⁷, Bi³⁸, Si^{39,40}, $Ge_{15}Te_{85}$ ⁴¹, liquid metals⁴², graphite⁴³ and BeF_2 ³⁴ shows thermodynamic anomalies³¹, while silicon⁴⁴ and silica^{33,35,36,45} show a maximum in the diffusion coefficient at constant temperature. These systems and their density and diffusion anomalies can be described in an effective way by a two length scale core-softened potential. This type of coarse graining model when used in dumbbell particles in which both monomers are identical and interact by two length scale potential shows the presence of liquid-crystal

type of order discribed above⁹.

Naturally given the production of silver-silicon janus the question arises what happens when a core-softened potential particle and an hydrophobic or an hydrophilic particles particle are jointed to form a dumbbell. Is the micellar Janus behavior dominant or is the liquid-crystal observed in two length scales dummbbells the main behavior? In order to answer to this question in this paper we study the two limits of this question. The first system is a dumbbell in which one monomer interact through a core softened potential with a very small attractive part and another monomer that is purely repulsive. The second system is a dumbbell in which one monomer interacts by a two length scales potential but the second shows attraction.

The paper is organized as follows: first we introduce the model and describe the methods and simulation details; next the results and discussion are given; and then we present our conclusions.

II. THE MODEL AND THE SIMULATION DETAILS

The system consists of N dimmeric nanoparticles, in a total of $2N$ monomers. The Janus dumbbells was modeled using two spherical symmetric particles, each one with mass m and both with an effective diameter σ , linked rigidly at a distance $\lambda = 0.8$. Three types of monomers were used. Monomers of type A interact with another monomer of type A through a core-softened (CS) pontential, while monomers of type B interact with another monomer B with a purely repulsive potential and monomers of type C interact with another monomer C through an attractive Lennard-Jones (LJ) potential. The two length scale potential that gives to the monomeric and dimeric system made only with particles A the anomalous characteristics is defined as⁴⁶

$$\frac{U^{AA}(r_{ij})}{\varepsilon} = 4 \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + u_0 \exp \left[-\frac{1}{c_0^2} \left(\frac{r_{ij} - r_0}{\sigma} \right)^2 \right] \quad (1)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between two A particles i and j . This equation has two terms: the first one is the standard 12-6 LJ potential⁴⁷ and the second one is a Gaussian centered at r_0 , with depth u_0 and width c_0 . Using the parameters $u_0 = 5.0$, $c = 1.0$ and $r_0/\sigma = 0.7$ this equation represents a two length scale potential, with one scale at $r_{ij} \equiv r_1 \approx 1.2\sigma$, where the force has a local minimum, and the other scale at $r_{ij} \equiv r_2 \approx 2\sigma$,

where the fraction of imaginary modes has a local minimum⁹. The cutoff radius for this potential is $r_c = 4.0$. Despite the mathematical simplicity, monomeric and dimeric fluids using this shoulder model does exhibit the density, the diffusion, and the response functions anomalies observed in water and other anomalous fluids^{46,48–51}.

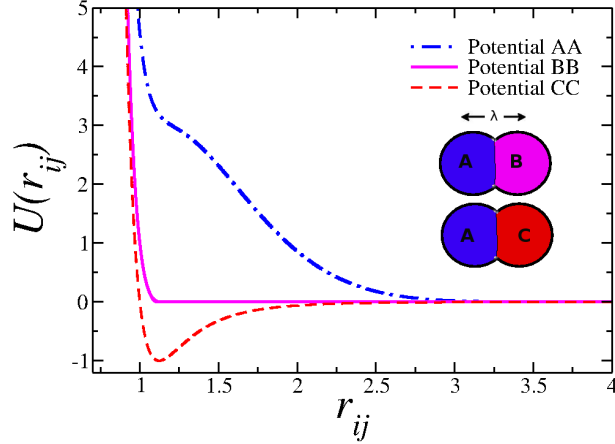


FIG. 1. Interaction potentials used in our simulations: the shoulder potential AA (dot-dashed blue line), the CSLJ potential BB with $r_c = 2^{1/6}$ (solid magenta line) and the CSLJ potential CC with $r_c = 2.5$ (dashed red line). Inset: Janus nanoparticles formed by A-B monomers and by A-C monomers.

The repulsive interactions are given by a cut and shifted Lennard-Jones (CSLJ) potential while the attractive particles interact by Lennard-Jones potential namely

$$U^{\text{CSLJ}}(r_{ij}) = \begin{cases} U_{\text{LJ}}(r_{ij}) - U_{\text{LJ}}(r_c), & r_{ij} \leq r_c, \\ 0, & r_{ij} > r_c. \end{cases} \quad (2)$$

Here, U_{LJ} is the standard 12-6 LJ potential, included in the first term of equation (1), $r_c = 2^{1/6}$ is the cutoff for the B-B interaction, namely potential BB, and $r_c = 2.5$ for the C-C interaction, namely potential CC. The first case model a purely repulsive excluded volume interaction, while the second one has a attractive well. The interactions between A-B, B-C and A-C monomers are also purely repulsive given by the equation (2) with $r_c = 2^{1/6}$. The potentials are shown in figure 1. The internal bonds between each dimer remain fixed using the SHAKE algorithm⁵².

Here we explore two model systems. In the first model the nanoparticles are composed by one monomer of type A and one monomer of type B, representing the combination of an

anomalous fluid with an hydrophobic system. In the second case, the dumbbell is modeled by a monomer of type A and one monomer of type C representing a janus particle in which one monomer is an anomalous fluid and the other is a very hydrophilic system. Both cases are illustrated in the inset of the figure 1.

Molecular dynamics simulations is used in order to obtain the pressure versus temperature ($p \times T$) phase diagram. The simulations were performed in the canonical ensemble using the ESPResSo package^{53,54}. A total number of 1000 particles (500 dimers) were used. The number density is defined as $\rho = N/V$, where $V = L^3$ is the volume of the cubic simulation box. Standard periodic boundary conditions are applied in all directions. The system temperature was fixed using the Langevin thermostat with $\gamma = 1.0$, and the equations of motion for the fluid particles were integrated using the velocity Verlet algorithm, with a time step $\delta t = 0.01$. We performed 5×10^5 steps to equilibrate the system. These steps are then followed by 5×10^6 steps for the results production stage. To ensure that the system was equilibrated, the pressure, kinetic energy and potential energy were analyzed as function of time, as well several snapshots at distinct simulation times. To confirm our results, in some points we carried out simulations with 2000 and 5000 particles, and essentially the same results were observed.

To study the dynamic anomaly the relation between the mean square displacement (MSD) with time is analyzed, namely

$$\langle [\vec{r}_{\text{cm}}(t) - \vec{r}_{\text{cm}}(t_0)]^2 \rangle = \langle \Delta \vec{r}_{\text{cm}}(t)^2 \rangle, \quad (3)$$

where $\vec{r}_{\text{cm}}(t_0) = (x_{\text{cm}}(t_0)^2 + y_{\text{cm}}(t_0)^2 + z_{\text{cm}}(t_0)^2)^{1/2}$ and $\vec{r}_{\text{cm}}(t) = (x_{\text{cm}}(t)^2 + y_{\text{cm}}(t)^2 + z_{\text{cm}}(t)^2)^{1/2}$ denote the coordinate of the nanoparticle center of mass (cm) at a time t_0 and at a later time t , respectively. The MSD is related to the diffusion coefficient D by

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta \vec{r}_{\text{cm}}(t)^2 \rangle}{6t}. \quad (4)$$

The structure of the fluid was analyzed using the radial distribution function (RDF) $g(r_{ij})$, and the pressure was evaluated with the virial expansion. In order to check if the Janus system shows density anomaly we evaluate the temperature of maximum density (TMD). Using thermodynamical relations, the TMD can be characterized by the minimum of the pressure versus temperature along isochores,

$$\left(\frac{\partial p}{\partial T} \right)_{\rho} = 0. \quad (5)$$

The fluid and micellar region in the $p \times T$ phase diagram were defined analyzing the structure with $g(r_{ij})$, snapshots and the diffusion coefficient D .

In this paper all the physical quantities are computed in the standard LJ units⁴⁷,

$$r^* \equiv \frac{r}{\sigma}, \quad \rho^* \equiv \rho \sigma^3, \quad \text{and} \quad t^* \equiv t \left(\frac{\epsilon}{m \sigma^2} \right)^{1/2}, \quad (6)$$

for distance, density of particles and time, respectively, and

$$p^* \equiv \frac{p \sigma^3}{\epsilon} \quad \text{and} \quad T^* \equiv \frac{k_B T}{\epsilon} \quad (7)$$

for the pressure and temperature, respectively, where σ is the distance parameter, ϵ the energy parameter and m the mass parameter. Since all physical quantities are defined in reduced LJ units, the $*$ is omitted, in order to simplify the discussion.

III. RESULTS AND DISCUSSION

A-B type nanoparticles

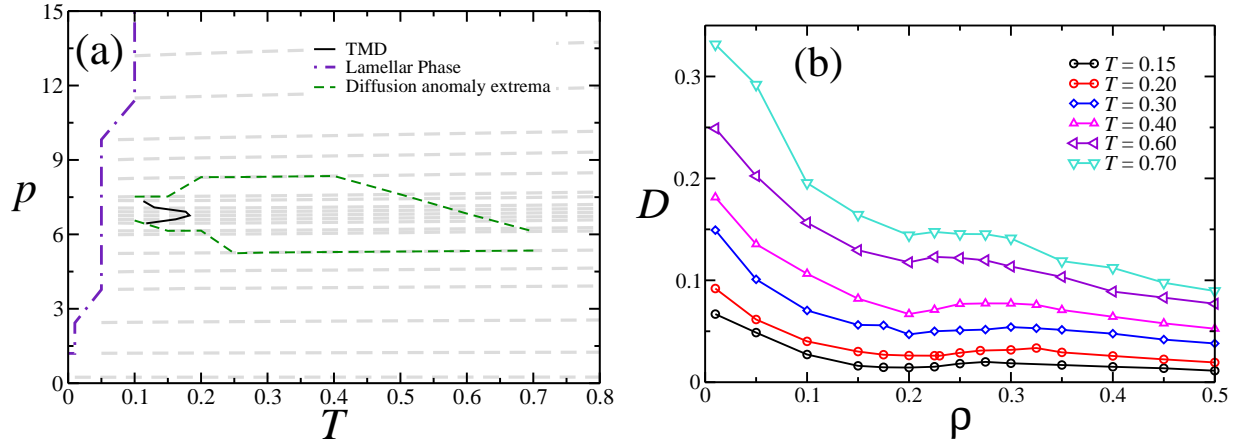


FIG. 2. (a) $p \times T$ phase diagram for the system composed by A-B Janus nanoparticles. The black line denotes the TMD line, the dashed green line the diffusion anomaly region extrema and the dot-dashed purple line the separation between the fluid and the lamellar phase. Grey lines are the isochores. (b) Center of mass diffusion coefficient D as function of density ρ for different temperatures, showing the diffusion anomaly.

We analyze a system of janus particles in which one monomer is of type A and the other is of type B, the AB system. Previous works⁴⁹ has shown that dimers with two

monomers of type A exhibit thermodynamic, dynamical and structural waterlike anomalies and a liquid-crystal lamellar phase. First, we focus in the thermodynamic (density) and dynamical (diffusion) anomalies.

The $p \times T$ phase diagram of this AB system is shown in the figure 2(a). This system exhibits a region of pressures and temperatures in which the density increases with the increasing density. The temperature of maximum density for different pressures is illustrated as a solid line in the figure 2(a). The points where obtained using equation 5. The diffusion coefficient versus density for different temperatures is shown in the figure 2(b). For some densities and temperatures, the diffusion coefficient, D , increases with ρ what characterizes an anomalous behavior. As a result for certain temperatures there is a minimum and maximum diffusion coefficient. These two points are illustrated as a bottom and an upper dashed lines in the pressure versus temperature phase diagram in the figure 2(a). Therefore the the region of the diffusion anomalous behavior in the pressure versus temperature phase diagram englobes the region of the density anomaly what is identified as hierarchy of anomalies. This hierarchy is also observed for the monomeric⁴⁶ and A-A dimers⁴⁹.

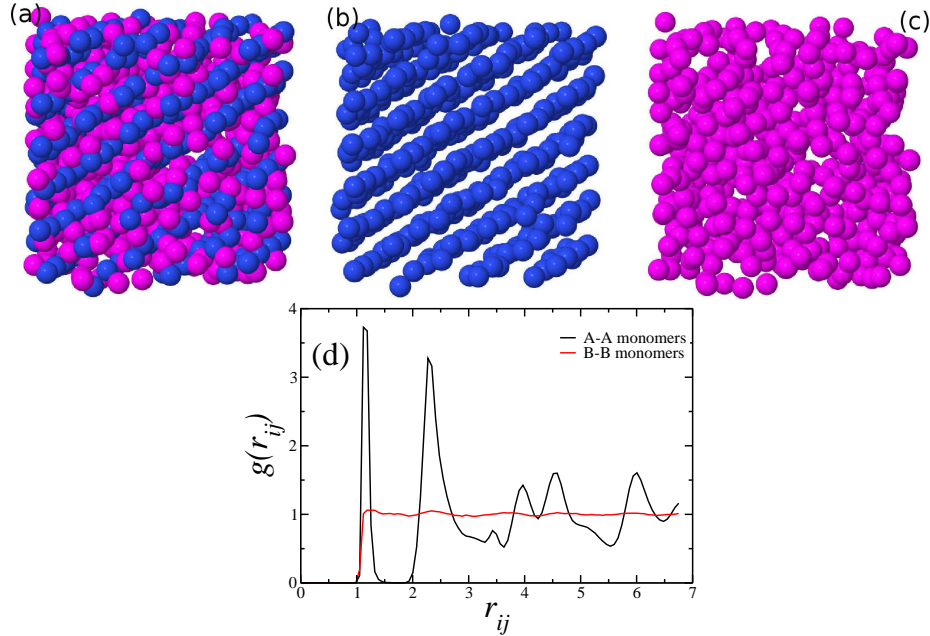


FIG. 3. (a) System snapshot in the lamellar phase, at $T = 0.1$ and $\rho = 0.4$ including all particles, (b) only the A (blue) monomers and (c) only the B (pink) monomers. (d) Radial distribution function for A-A pairs (solid black line) and B-B pairs (solid red line).

The fluid-solid separation occurs at lower temperatures compared with the A-A case⁴⁹, mainly due the excluded volume by B monomers. In the fluid phase, no ordering was observed. In the solid region, defined when the fluid is structured and with $D \approx 0$, the system is structured in a lamellar micelle. The figure 3(a) shows a snapshot of the nanoparticles in this region, at $T = 0.1$ and $\rho = 0.4$. To clarify the structure we analyze the A and B monomers separately. Figure 3(b) and (c) are snapshots of A monomers and B monomers, respectively. As we can see, the A monomers are in a lamellar well defined structure, while the B monomers are disordered, with a fluid-like behavior. Since the center of mass diffusion coefficient is approximately null, this indicates that the A monomers are fixed in the lammelar structure, while the B monomers are spinning around the A monomers, in a fluid-like behavior. The radial distribution function for this point, shown in figure 3(d), reinforces this conclusion. The RDF for A monomers is characteristic of a solid, and for B monomers is clear the RDF of a gas. For all densities and temperatures simulated only this lamellar structure was observed in the solid phase. The snapshots and RDF for this points are omitted for simplicity.

The hard sphere-two length scales dumbbell forms a plane of two length scales monomers as illustrated in the figure 3(b). In the case of a dumbbell in which both monomers interact through a two length scales potential the two monomers minimize the free energy by being apart a distance $d \approx 2\sigma$ between the lines. Inside each line the distance is $d_1 \approx 1\sigma$

The reason for this difference is that while the two length scales particles minimize the free energy being either at $d \approx 2\sigma$ e $d_1 \approx 1\sigma$, the hard core monomers are limited by the hardcore distance. The combination of these two particles that are linked by the dumbbell leads to the appearance of the planes.

Another effect from the Janus characteristic of the nanoparticle is that the liquid-crystal phase observed for A-A dimers was not observed in the A-B case. Once the anomalies are preserved, our results indicates that in the A-B case the two length scales potential determines three fluid behavior.

A-C type nanoparticles

Next, we analyze the A-C Janus dimers. Replacing the purely repulsive B monomer by the attractive C monomer leads to changes in the pressure versus temperature phase diagram

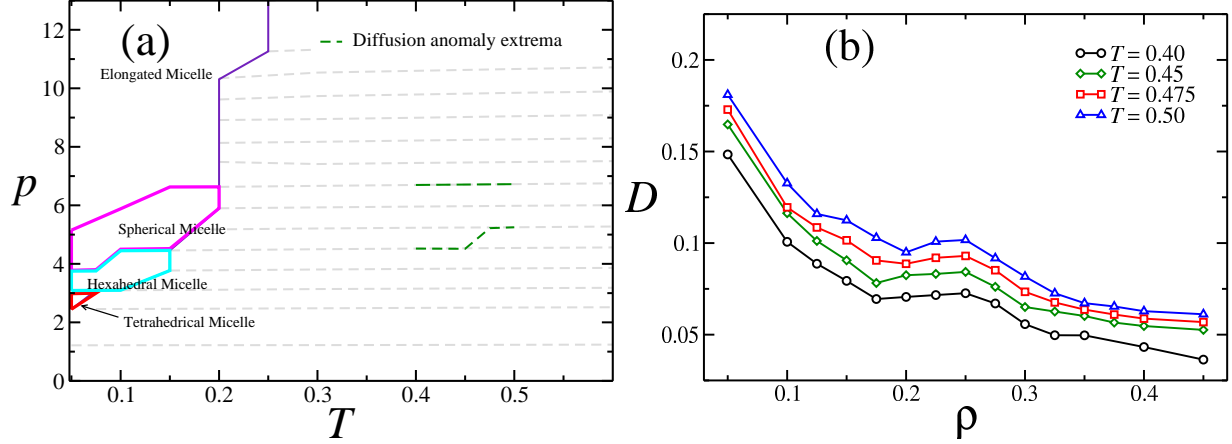


FIG. 4. (a) $p \times T$ phase diagram for the system composed by A-C Janus nanoparticles. The dashed green line the diffusion anomaly region extrema and the distinct micellar regions are depicted in the graphic. Grey lines are the isochores. (b) Center of mass diffusion coefficient D as function of density ρ for different temperatures, showing the diffusion anomaly.

when compared with the A-B case. As we show in figure 4(a), the density anomaly disappears and the diffusion anomaly regions shrinks. The diffusion anomalous increase as the system is compressed is shown in figure 4(b) for isotherms between $T = 0.4$ and 0.5 – the region where the anomaly was observed. The waterlike anomalies can be related with the particles separation, at a higher distance with small energy, or at a smaller distance and higher energy - the two length scales in the equation (1)⁹. The particles moves to the closest configuration, the first length scale, as we increase the temperature - or increase the entropic contribution to the free energy, while the enthalpic contribution to the free energy is higher when the characteristic distance is the second length scale. The competition between the two length scales, or between entropy and enthalpy, leads to the waterlike anomalies⁵⁵. Therefore, the suppression of the density anomalous region and the the occurrence of diffusion anomaly only at high temperatures are consequence of the attractive interaction, witch favors the enthalpic contribution to the free energy.

Another difference from the A-B nanoparticles are the self-assembled structures. While for the first case only a lamellar phase was observed, for A-C monomers we obtained four different micelles structures. The micellation temperature is higher than in the previous case, as expected for attractive particles. To analyze the micellar phase we will discuss

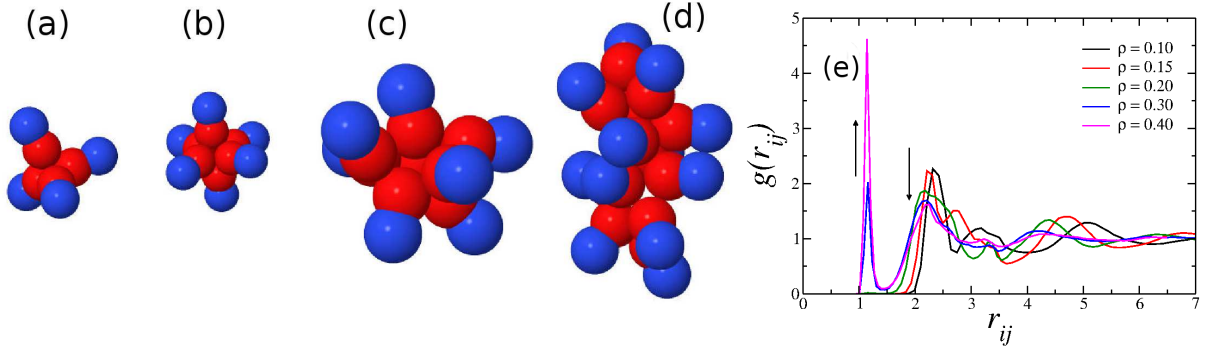


FIG. 5. System snapshot in the micellar phase, at $T = 0.05$ and (a) $\rho = 0.10$, (b) 0.15, (c) 0.20 and (d) 0.30, respectively, showing the distinct self-assembled micelles: tetrahedral, hexahedron, spherical and elongated, form left to right. (e) Radial distribution function for A-A pairs at temperature $T = 0.05$ and for different densities, showing the competition between the length scales. The arrows indicates the behavior of each peak as the density increases.

the temperature $T = 0.05$, where all structures were observed. At small pressures, in the region limited by the red line in the figure 4(a), the dumbbells are structured in pyramidal tetrahedral clusters, similar to the water tetrahedral cluster, with the C monomers attached and pointing to the center of the cluster. For higher pressures, inside the region limited by the cyan line in the figure 4(a), the nanoparticles are in a hexahedron structure, composed by six dimers with the C monomers pointing to the center of the structure. These structures are shown in figures 5(a) and 5(b) for the temperature $T = 0.5$ and density $\rho = 0.10$ (tetrahedral) and $\rho = 0.15$ (hexahedron). Increasing the density, as $\rho = 0.20$, more dimers attach to the micelles, and the structure changes from a hexahedron to a spherical micelle. This structure was observed inside the region limited by the magenta line in figure 4(a). Finally, at even higher densities, as $\rho = 0.30$, the high pressure changes the micelles shape from spherical to elongated micelles, as shown in figure 5(c) and 5(d). The transition between tetrahedral – hexahedron – spherical micelle can be understood by the fact that increasing the density (and consequently the pressure) more C monomers will be attached in a micelle, changing the structure shape. However, the spherical to elongated micelle transition is led by the competition between the two length scales in the anomalous potential. The RDF between A monomers, displayed in figure 5(e), shows that, in the density range were the

first three species of micelles were observed, all A monomers are at the second length scale, $r_{ij} \approx 2.0$, or further, while the first characteristic length scale, at $r_{ij} \approx 1.2$, do not have any occupancy. However, when the system is structured in elongated micelles the first length scale sharply increases, showing that the particles moved from the second length scale to the first one.

The presence of the self-assembled phases not present in the A-B and A-A cases are not surprising. They are present in the usual hydrophobic-hydrophilic janus particles. These phases are a result of the competition between the repulsion of the core-softened potential and the attraction of the LJ. As in the competing interaction models, all the transitions including the transition between the fluid to structured phases are first-order.

IV. CONCLUSION

In this work we have analyzed the pressure versus temperature phase diagram of a Janus dumbbells system comparing the effects of the competition between two length scales potential and an repulsive and attractive potentials. Each nanoparticle was composed by one anomalous monomer modeled with a two length potential and one monomer modeled as a standard LJ particle.

We found that when the only competition is between the two length scales, the system only shows the lamellar phase defined by the core-softened potential. In this case as in the pure CS dumbbell, density and diffusion anomalies are present in the pressure versus temperature phase diagram. In the case of the CS-attractive LJ dumbbell, the attraction affects the competition that lead to waterlike anomalies. As consequence, the density anomaly vanishes and the diffusion anomaly region shrinks. Also, the models shows a rich variety of micelles in self-assembly process similar to the behavior observed in the hydrophobic-hydrophilic janus dumbbell. Due to the attraction between C monomers and the two length scales competition between A monomers the nanoparticles can assembly to tetrahedral, hexahedron, spherical or elongated micelles.

Our results indicated that is possible to create distinct colloidal particles that will have waterlike anomalies and different micellar conformation. Further investigations of Janus dumbbells, including distinct LJ well depthness, monomers size and separation, are currently in progress.

V. ACKNOWLEDGMENTS

We thank the Brazilian agencies CNPq, INCT-FCx, and Capes for the financial support. We also thank to TSSC - Grupo de Teoria e Simulação em Sistemas Complexos at UFPel for the computational time in Satolep cluster.

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